

ELECTRONIC AND CHEMICAL PROPERTIES OF CYANATED,
HALOGENATED AND THIOPHENE-BASED LINEAR ACENE DERIVATIVES
BY FIRST-PRINCIPLES CALCULATIONS

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HALOGENATED AND THIOPHENE-BASED LINEAR ACENE DERIVATIVES
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The work is dedicated to my parents, family and the humanity

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ABSTRACT

Molecular modeling plays an essential role in searching for new and better organic electronic materials with excellent electronic and chemical properties to design organic electronic devices. In this research, we have studied some electronic, chemical and vibrational properties of linear acenes (from benzene to heptacene), and the additional effect of halogens, cyanate, and thiophene to linear acenes. The possible molecular properties of linear acenes and their derivatives as a function of a number of the fused benzene rings and the total number of carbons were studied. The computation is carried out using NWchem 6.3 code and Molden for molecular structure visualization. Hartree-Fock (HF), Density Functional Theory (DFT) and Møller-Plesset (MP2) level of the theories with B3LYP exchange functional using 6-311G, 6-311G (d,p), 6-311G* and aug-cc-pvdz basis sets are used for calculations. The ground state energy and band gap energy decrease with number of linear acene rings while the nuclear repulsion energy and Coulomb potential increase due to the accumulation of electrons in the bonding states. Additionally, π -bonding electrons increase the highest occupied molecular orbitals (HOMO) energy, and π^* -antibonding electrons decrease the lowest occupied molecular orbitals (LUMO) energy with the increase of the acene rings. The π -bonding electrons cause the resonance by delocalization of electrons around the linear acenes molecular structures. It was found that the band gap energy, chemical potential, μ and global hardness, η decrease with the increase in the number of acene rings whereas the electronegativity χ , softness S and electrophilicity ω increase with the number of linear acene rings. The results show good agreement with theoretical and experimental values. In addition, HOMO and LUMO orbitals energy, ionisation energy, electron affinity and global indices reveal that higher linear acene rings and their derivatives exhibit excellent electronic and chemical properties. However, due to high values of HOMO orbitals energy and low values of LUMO energy lead to low ionisation potential and high electron affinity across the acene derivatives which demonstrate that the materials have more potential application in organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs) than in optical application.

ABSTRAK

Pemodelan molekular memainkan peranan yang penting dalam usaha mencari bahan elektronik organik yang baharu dan yang lebih baik serta mempunyai sifat elektronik dan kimia yang sangat baik bagi merekabentuk peranti elektronik organik. Dalam penyelidikan ini, kami telah mengkaji beberapa sifat elektronik, kimia dan kegetaran bagi asin lurus (daripada benzin kepada heptasina), dan kesan tambahan halogen, sianat dan tiofen ke atas asin lurus. Sifat molekular yang mungkin bagi asin lurus dan terbitannya sebagai fungsi beberapa cantuman cincin benzin dan jumlah bilangan karbon turut dikaji. Pengiraan telah dilakukan menggunakan kod *NWchem 6.3* dan *Molden* untuk penggambaran struktur molekular. Hartree-Fock (HF), Teori Kefungsian Ketumpatan (DFT) dan teori aras Møller-Plesset (MP2) dengan fungsi penukaran B3LYP menggunakan set asas 6-311G, 6-311G(d,p), 6-311G* dan aug-cc-pvdz telah diguna untuk pengiraan. Jumlah tenaga keadaan dasar dan jurang tenaga berkurangan dengan bilangan cincin asin lurus, manakala tenaga tolakan nuklear, dan keupayaan Coulomb telah bertambah disebabkan oleh pengumpulan elektron dalam keadaan terikat. Sebagai tambahan, ikatan- π elektron meningkatkan tenaga penguasaan tenaga tertinggi orbital molekular (HOMO), dan antiikatan- π^* mengurangkan penguasaan tenaga terendah orbital molekular (LUMO) seiring dengan peningkatan cincin asin. Ikatan- π elektron meningkatkan resonans melalui pemisahan elektron di sekeliling struktur molekul asin lurus. Selain itu, turut ditemui, tenaga jurang jalur, keupayaan kimia, μ dan kekerasan global, η berkurangan seiring dengan pertambahan bilangan cincin asin manakala keeloktronegatifan, χ , kelembutan, S , dan elektrofilik, ω , bertambah dengan bilangan cincin asin. Keputusan ini telah menunjukkan terdapat kesamaan antara nilai teori dan eksperiment. Tambahan pula, tenaga-orbital HOMO dan LUMO, tenaga pengionan, afiniti elektron, dan indeks global telah mendedahkan bahawa cincin asin lurus yang tinggi dan terbitannya memaparkan sifat elektronik dan kimia yang sangat baik. Walau bagaimanapun, disebabkan oleh nilai tenaga orbital HOMO yang tinggi terhadap nilai tenaga HOMO yang tinggi dan nilai tenaga LUMO yang rendah telah membawa kepada potensi pengionan yang rendah dan afiniti elektron yang tinggi merentasi terbitan asin menjadikan bahan tersebut lebih berpotensi digunakan dalam peranti *organic light emitting diodes* (OLEDs) dan *organic field effect transistors* (OFETs) berbanding peranti optik.

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LIST OF SYMBOLS

μ	-	Chemical Potential
η	-	Global Hardness
χ	-	Electronegativity
S	-	Global Softness
ω	-	Electrophilicity
α_{tot}	-	Average polarizability
α_{xx}	-	Polarizability tensor along xx -direction
α_{yy}	-	Polarizability tensor along yy -direction
α_{zz}	-	Polarizability tensor along zz -direction
$\Delta\alpha$	-	Optical anisotropy polarizability

LIST OF ABBREVIATIONS

BFU	-	Bifuran
CIS	-	Configurational Interaction
DC-NAP	-	Dicynonaphthacene
DC-PEN	-	6, 13-dicyclopentacene
DFT	-	Density Functional Theory
EA	-	Electron affinity
eV	-	Electron volt
EMSL	-	Environmental Molecular Science Laboratory
FOE	-	Frontier orbital energy
GGA	-	Generalized Gradient Approximation
GSE	-	Ground state energy
HOMO	-	High Occupied Molecular Orbital
IP	-	Ionization potential
IR	-	Infrared
K.E	-	Kinetic energy
LCAO	-	Linear combination of atomic orbital theory
LDA	-	Local Density Approximation
LUMO	-	Lowest Occupied Molecular Orbitals
MO	-	Molecular Orbital
MP2	-	Møller–Plesset perturbation theory second order
MO	-	Molecular orbitals
NWchem	-	Northwest chemistry
OFETs	-	Organic field effect transistors
OLED	-	Organic light emitting diode
OSM	-	Organic Semiconductor Material
PAHs	-	Polyaromatic hydrocarbons
PES	-	Potential energy surface

RHF	-	Restricted Hartree-Fock
SCF	-	Self-consistent field theory
TDDFT	-	Time dependent density functional theory
TFU	-	Tetrafunan
XC	-	Exchange correlation
ZINDO	-	Zerner's intermediate neglect of diatomic differential overlap

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CHAPTER 1

INTRODUCTION

1.1 Overview

The chapter gives an introduction to the organic semiconductor and their application in molecular and organic material, the background of the study, problem statement, objectives of the research, the scope of the study, the significance of the work as well as the thesis outline.

1.2 Background of the Study

Interest in π -conjugate organic semiconductor materials has potentially increased over a decade in materials science as well as in chemistry and space physics. This is due to their promising advantages over a traditional inorganic material such as lower cost of production, light weight, flexibility (see Figure 1.1), large area of coverage such as in nanomaterials (Nicolas *et al.*, 2012), low temperature and soluble-based processes (Fahem and Bauhofer, 2012), and promising mechanical properties (Cosseddu *et al.*, 2013).

The π -conjugate organic materials also demonstrate significant important applications in organic light emitting diode (OLED), energy storage, photovoltaic cells, organic thin film transistors (OTFT), electrochromic devices, sensors (Ozen *et al.*, 2011), electronic paper and flat panel liquid crystal displays (Ruiz *et al.*, 2005)

and organic electrochemical transistor as biocompatible for brain-machine interface (Khodagholy *et al.*, 2013), and their application in rechargeable Li-ion batteries (Firouzi and Zahedi, 2008). They are utilized in glassy carbon materials and graphene sheets (Hajgató *et al.*, 2008). Also, Nall (2011) has described the most applicable areas of application of organic semiconductor materials such as; active-matrix OLED, organic light emitting diode, organic field-effect transistor, organic solar cell and hybrid solar cell.

In addition, low-cost ‘smart cards’, radio-frequency ID tags and printable transistors are under active investigation (Ruiz *et al.*, 2005). Also, due to good quantum fluorescence efficiency and high mobility of hole transport, the acene derivatives are the most promising candidates for optoelectronic devices application; this includes organic light emitting diodes, organic field effect transistor and hole collectors in organic photovoltaic cells (Pan *et al.*, 2008).

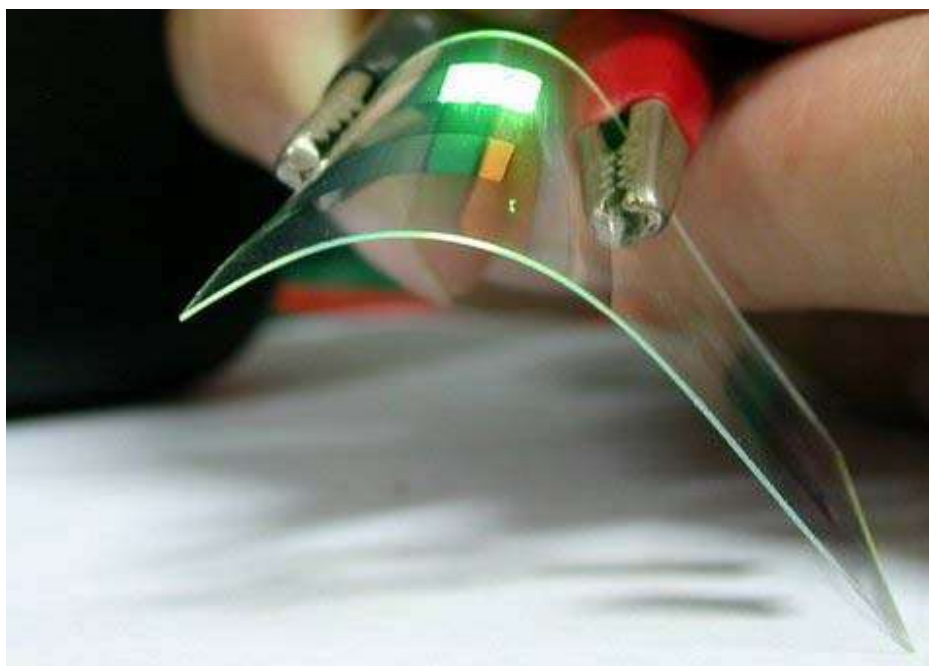


Figure 1.1: Demonstration of a flexible OLED device

(Source: solar.upsttime.com/oled-power-new-screens-are-solar-panels)

However, organic semiconductor materials are divided into two broad groups: oligomers (small molecules); these are chemically or industrially treated in a vacuum, and the polymers, which are mainly treated by wet chemical techniques. The oligomers and co-oligomers have demonstrated some promising results over a polymer. Thus, they are easily soluble in organic solvents, distilled and formed a crystalline film. Oligomers and co-oligomers of thiophenes and acenes are essential molecules for OFETs device (Zhao *et al.*, 2013). Also, some theoretical findings in the same study have shown that oligoacene of anthra [2, 3-c] thiophene and their cyanate derivatives manifested ultra-low hole reorganization energy which suggests oligoacene materials to be excellent candidates for p-type semiconductors.

Consequently, organic semiconductor materials utilized molecular orbitals (MO) as the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO); a probable electronic state of organic material. This is a transition state for π -electrons in organic molecules. The HOMO and LUMO orbitals energy of the organic semiconductor play an important role in determining the electronic and optical property of the π -conjugate organic materials (Sun, 2006).

Also, another property that determines the material property is; ionization potential (IP) and the electron affinity (EA). The material with p-type or n-type organic material conduction; the ionization potential, IP and electron affinity, EA is mainly used to estimate the energy barrier for injection of holes and electrons, and to determine the efficiency of the material for molecular device design (El-Nahas *et al.*, 2012). However, for an efficient electron injection from standard metal electrodes, the minimum value of electron affinity (EA) should be 3.00 eV (Purushotham and Sastry 2013).

1.3 Problem Statement

Research and Industrial applications show that oligomers of acenes, their derivatives, heterocyclic hydrocarbons and their polymers have been under intensive study over a decade, after the discovery of the first organic semiconductor material by Shirakawa (Shirakawa *et al.*, 1977). In addition, prediction of a new material is now being employed via modelling and computational methods, which yields remarkable results where the experimental methods become difficult and expensive to carry out.

However, there are many impending challenges regarding the development of an organic semiconductor material application with linear acenes. In general, Garzón *et al.* (2010) have observed the problems with the molecular design of organic semiconductor material that they have a poor concentration of electrons, scarcely soluble, which is difficult to process. Also, they are also unstable in air. In addition, García *et al.* (2011) have reported that the luminescence, electroluminescence and electronic property of n-type organic material is affected when subjected to air, whereas the p-type organic material behave differently and show an increase in material conductivity with the air pressure.

On the other hand, García *et al.* (2012) have reported in their study of poly(arylenethynyl-thienoacenes), a linear acenes derivative for optoelectronics devices that the main problems with ambipolar organic semiconductors is the intrinsic instability of radical ions in the air, and the high barrier for electron injection, which considered to be the work function used as noble metals. Also, a similar case related pentacene and other high linear acene molecules were reported by (Wang *et al.*, 2012).

Further, (Shinamura *et al.*, 2011) have demonstrated that pentacene is an ideal organic semiconductor material for organic field effect transistor (OFET), but high oxidation potential and chemical instability defined by the HOMO energy level makes the molecules susceptible to air oxidation. This is also a major setback for its further practical application. Similarly, Bunz (2015) has observed a similar case that

linear acenes with high ring such as hexacene and heptacene experienced insolubility and high reactivity, which make them difficult to process.

However, many attempts have been made to overcome the above challenges in the design of an organic and molecular electronic device. The early report for an air-stable organic semiconductor was the use of Bis (dithienobenzene), a benzene derivative with reasonable exhibited thin-film mobility of $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Wang *et al.*, 2012). Also, Tang and Bao (2010) have reported that the use of halogen (such as fluorine, chlorine and bromine etc) in the acenes molecule could be the best method forward to overcome the instability in the air that is beneficiary toward a proper commercialization of organic semiconductor devices. Thus, the method resulting in production of n-type organic materials.

Moreover, Katsuta *et al.* (2011) have reported another improvement for air stability organic semiconductor with tetracene and pentacene using cyanate for OFET performance; 5,12-dicynonaphthacene (DC-NAP) and 6,13-dicynopentacene (DC-PEN) material, a linear acene derivatives. The result demonstrated the improvement toward air stability of the molecules. In addition, the HOMO and LUMO level differences for DC-NAP and DC-PEN is 0.83 eV and 0.89 eV, and 4.0 eV and 4.14 eV with the LUMO level similar to that of fullerene, C_{60} respectively. Due to anionic states and low LUMO level, both DC-NAP and DC-PEN behave as n-type organic semiconductors. Pramanik and Miller (2012) have reported a different procedure for the synthesis of pentacene-based acenes with an effort to integrate pentacene to OLEDs and photovoltaic devices.

Furthermore, Watanabe *et al.* (2013) have cited that other bulk materials are utilized to increase the charge and controlling stability of organic semiconductor materials such as arthio, phenyl, alkylsilylethynyl and many others. Also, the replacement of hydrogen in carbon-hydrogen bond, -CH group in the acenes family (azaacenes) backbone with hetero atoms has additionally advanced the scientists to modify their properties. This has strongly transformed the frontier orbitals energy (FOE) structure of new organic molecular structures by their number, position, and

valencies toward the enhancement of molecular material design (Li and Zhang, 2015).

In addition, Zhang *et al.* (2013a) have reported that other parameters can be applied to evaluate properties related to molecular stability and the production of charges, such as ionization potential and electron affinity. It is shown that a molecule with higher ionization potential indicates a better stability of the material, whereas a smaller electron affinity reveals the large barrier for electron injection, which is also a remarkable way of manipulating the molecules to improve electronic efficiency.

Also, with the exact or local density approximation (LDA), generalized gradient approximation (GGA) models, recently have provided good representation and physical meaning of the optical band gap E_{gap} and frontier orbitals energy, which is usually determined by optical spectroscopy experimental (Baerends *et al.*, 2013)(Cardia *et al.*, 2014; Autschbach and Srebro, 2014).

Despite the fact, there many literature that have reported on the properties of linear acenes and their derivatives, and synthesis, but not all accounts for their chemical properties by quantum chemical indices. Also, in some studies, the ground state energy, electronic and vibrational properties of the linear acenes and their derivatives were not comprehensively studied.

However, due to their significance in organic and molecular electronic materials, there is a need to further study their properties for the potential used in organic semiconductor materials design. Hence, in this research work, we will report and extend the study of electronic, chemical and vibrational properties of linear acenes, and to predict their derivatives based on the previous literature. Also, Hartree-Fock (HF) method, Density Functional Theory (DFT) with B3LYP exchange correlation and MP2 with a selected basis set will be used. This will be given a clear justification on the results in comparison to previous work.

1.4 Research Objectives

The primary aim of the research is to investigate, calculate and predict through chemical physics study, the properties of linear acenes that have potential applications in molecular device design such as OFETs and OLEDs. To accomplish the above aim the specific objectives are proposed as follows:

- 1) To calculate the ground states energy and electronic properties of linear acenes ($n = 1$ to 7) compounds by linear combination atomic orbitals theory (LCAO) at HF, DFT-B3LYP and MP2 methods. Also to compute their excited electronic states using TDDFT.
- 2) To compute the chemical properties using quantum chemical indices for the linear acenes that are useful to the design of OLEDs and OFETs materials. Some of the parameters include ionization energy (IE), electron affinity (EA), chemical potential (μ) and global hardness (η) etc.
- 3) To determine the vibrational properties of linear acenes relevant to the organic semiconductor materials application.
- 4) To identify the above said properties for linear acene derivatives based on substitution of halogen, cyanate and thiophene-based. As the present method for enhancement of acenes properties use in molecular and organic electronic application.

1.5 Scope of the Study

In this research work, a linear combination atomic orbital (LCAO) method is adopted to calculate electron, chemical and vibrational properties of linear acenes ($n = 1$ to 7) and the prediction of their derivatives based on the addition of cyanate, halogen, and heterocyclic compounds. Energy minimization and structure optimization will be carried out with NWchem 6.3 code (Aprà *et al.*, 2003; Valiev *et*

al., 2010) under the DFT theory at B3LYP exchange. The following approaches are adopted to calculate electronic, chemical and vibrational properties of linear acenes ($n = 1$ to 7) and their derivatives:

- (a) Atomic coordinates, ground state energy, Coulomb potential, nuclear repulsion energy and infrared vibrational frequency parameter can be calculated with the help of energy minimization procedure using Hartree-Fock and density functional theory (DFT) approximations.
- (b) Electronic properties such as HOMO energy, LUMO energy and band gap energy, and their excited state (S_1) etc. can be computed using Hartree-Fock (HF), density functional theory (DFT), MP2 approximations, and time dependent density functional theory (TDDFT) with B3LYP exchange-correlation.
- (c) Global quantum chemical indices like chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S), electrophilicity (ω), ionization potential (IP), and electron affinity (EA) can be utilized to predict and analyse the chemical stability of the molecular structures.
- (d) Vibrational property such as infrared spectra can be evaluated by using DFT approximation at B3LYP exchange.
- (e) To overcome the problem of convergence in optimization of the total ground state energy and electronic properties, different basis sets like 6-311G, 6-311G (d, p), 6-311G* etc. are used for accurate predictions.

1.6 Significances and Original Contribution of the Study

The study of linear acenes ($n = 1$ to 7) properties; benzene, naphthalene, anthracene, tetracene, pentacene, hexacene, heptacene, and the prediction of their derivatives by first-principle calculations using LCAO method is an attempt to contribute to the existing knowledge on linear acenes electronic, chemical and vibrational properties. Also, the findings of this study would make a necessary recommendation that eventually lead to the potential application of the studied materials for the development of the molecular and organic electronic device design. The important achievements in the study are:

- (i) Hartree-Fock (HF), Density functional theory (DFT), (MP2) and CAM-B3LYP with B3LYP exchange-correlation using LCAO method are utilized simultaneously to remove the discrepancy in the results associated with the properties of linear acenes ($n = 1$ to 7).
- (ii) The designated ranges of the molecular structures have never been part of any first-principle calculations until current study. Electronic, chemical, and vibrational parameters and prediction of new molecular derivatives of linear acenes are calculated and predicted first time.
- (iii) The present research work proves that the addition of halogen, cyanate, and heterocyclic functional atoms or molecules to linear acenes molecular structures is a good method to increase and improve the stability, and electronic properties of the linear acenes.
- (iv) Selected quantum chemical indices such as chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S), electrophilicity (ω), ionization potential (IP), and electron affinity (EA) are utilized for the first time to establish chemical instability of the linear acenes and their derivatives. The study has proven that the linear acenes; naphthalene to pentacene and their derivatives are useful for OLEDs and OFETs design.

- (v) The frequencies vibrational spectra relevant to molecular absorption are also established and analysed first time for the linear acenes and some of their derivatives. Also, wavenumbers in the infrared regions of transmittance intensity are identified.

1.7 Thesis Structure and Organization

Chapter 1 captures the general introduction of the research work, which includes research background, research problems that need to be addressed in the work, objectives, and scope of the research, and as well as the importance of the study and the thesis structure organization.

Also, Chapter 2 reviews the literature on polyacenes (linear acenes) and their derivatives, and also heterocyclic compounds. In addition, Chapter 3 discusses the methodology involved in the research work. Theoretical framework and the methods, as well as computational details of the research work, are given in chapter three.

Chapter 4 discusses the results including, calculation of ground state energy (GSE), electronic properties, optical excitation, etc. Also, Chapter 5 discusses on chemical indices like; chemical potential (μ), electrophilic (ω), global hardness (η), electronegativity (χ), global softness (S), and vibrational properties. Finally, Chapter 6 summarizes and reported the conclusion of the research work. Also, research limitation, reference list, and appendices are listed in the chapter accordingly.

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